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### COMPLETE SPECIFICATION

## Process of and Apparatus for the Refining Treatment of Relatively Low Boiling Cracked Hydrocarbons

(A communication to me from abroad by the UNIVERSAL OIL PRODUCTS COMPANY, a corporation duly organised under the Laws of Delaware, of 310, South Michigan Avenue, Chicago, State of Illinois, United States of America).

I, ALBERT LEVY MOND, Doctor of Science, of the University of Geneva, Chemical Engineer and Patent Agent, of 19, Southampton Buildings, Chancery Lane, London, W.C.2, British Subject, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to the treatment of the lower boiling gasoline-containing distillates produced as a result of cracking operations upon heavy hydrocarbon oils.

More specifically it embodies a process of treatment involving closely co-operative steps leading to the production of a stabilised gasoline which is substantially free from gum and resin-forming constituents and requires little, if any, further chemical or physical treatment to render it utilisable as a motor fuel.

In the earlier stages of the development of the cracking art and up to a comparatively recent date, the prevailing practice in refinery operations involving cracking was to produce a crude naphtha, which contained all the gasoline boiling range fractions, as well as fractions of lower and higher boiling ranges, and to subject this naphtha to treatment with various chemical treating reagents, particularly sulphuric acid, to treat out readily polymerisable materials and reduce the sulphur content to a permissible percentage. After chemical treatment the properly neutralised naphtha was redistilled with steam to insure a low temperature distillation and avoid decomposing soluble treating products and the overhead fraction comprising the finished gasoline, subjected to a caustic wash to remove any residual acidity.

The inherent disadvantages in this procedure were in time recognised, these

being the cost of chemicals, the inconvenient and frequently cumbersome methods of chemical treatment and the need for redistilling which required a large amount of heat and special distillation equipment. Attempts were then made to produce a finished gasoline directly from the cracking plant by treating the vapours with different chemicals. These processes have only met with partial success.

In the more recent practice of refining, cracked hydrocarbon distillates of substantially gasoline boiling range produced by condensing the final overhead vapours from a fractionation of vapours of a cracking operation are employed as the charge to be subjected to the refining treatment. In the refining of such cracked hydrocarbon distillates in the liquid phase at elevated temperature with a solid active adsorbent such as charcoal, fullers earth or like porous material, owing to the presence of gases and unstable low boiling constituents and their vapour tension at the elevated temperature at which the treatment is performed, an excessive pressure is required for maintaining the hydrocarbons in liquid phase which entails unnecessary power. Moreover the presence of the unstable low boiling constituents combined with the excessive pressure cause an undesired extent of polymerisation, and owing to the larger volume of hydrocarbons to be treated the efficiency of the adsorbent is reduced.

In order to overcome these disadvantages, in the process of the present invention relatively unstable low boiling constituents, namely dissolved gases, propane, part or all of the butanes and their corresponding unsaturates are removed from cracked hydrocarbons of substantially gasoline boiling range and the vapour pressure of said hydrocarbons is reduced by a stabilising fractionation prior to the refining treatment with the solid active adsorbent. Moreover, in order to render such refining treatment practical and commercially advantageous, said stabilising fractionation and the adsor-

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bent treatment are effected in such a way that the stabilised hydrocarbons are submitted to said refining treatment whilst still in a hot condition.

- 5 In one mode of operating the process of the invention the production, by fractionation, of a fraction of substantially gasoline boiling range from vapours from a cracking operation may be combined  
10 with the stabilising fractionation of such fraction; the stabilised fraction of substantially gasoline boiling range is in this case withdrawn as hot condensate from an intermediate point of the combined  
15 fractionation and, without cooling, subjected to the action of the solid active adsorbent. In another mode of operating the process of the invention, the stabilising fractionation may be effected separately  
20 from the fractionation for producing the hydrocarbons of substantially gasoline boiling range from vapours from a cracking operation. Heavier reflux condensate obtained in the latter fractionation may  
25 be returned to the cracking process for further conversion, if desired, after its utilisation as a source of heat for the reheating of the gasoline-like fraction passing to, or issuing from, the refining treatment with the solid active adsorbent.  
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The action of the solid active adsorbent on the stabilised fraction is preferably effected at a temperature of from 300 to 450°F. and under a superatmospheric  
35 pressure of about 250—500 pounds, or more, per square inch.

The attached drawing is a diagrammatic side elevational view of one form of apparatus in which the process may be  
40 conducted.

Referring to the drawing, the first unit shown is a fractionator of a cracking plant, the vapours from the cracking or preliminary fractionating zone entering fractionator 3 by way of line 1 containing  
45 control valve 2, the pressure of the cracking plant being usually reduced at this point to say, 50 to 100 pounds per square inch. The function of this fractionator is to produce a distillate containing substantially all of the gasoline boiling  
50 range compounds and a reflux material which may be returned to the heating element of the cracking plant as a portion of the combined feed.  
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Vapours from the fractionator pass through line 4 containing control valve 5, the liquefiable portions being condensed by passing through condenser 6 and flowing  
60 thence by way of line 7 containing control valve 8 to a receiver 9 provided with gas release line 7' and control valve 8'. In order to control the fractionation, a portion of the distillate produced at this  
65 point is taken by pump 12 by way of line

10 containing control valve 11 and discharged back into the top of the tower by way of line 13 containing control valve 14.

The next step in the process involves the stabilisation of the distillate in respect to its high vapour pressure constituents such as dissolved gases, propane, and a portion of the butanes, and for this purpose the distillate is revaporised and  
70 subjected to a carefully controlled pressure fractionation. Pump 17 takes suction upon the distillate in receiver 9 through line 15 containing control valve 16 and discharges through line 18 containing  
75 control valve 19 through heating element 20 positioned in furnace 21. The heated products are discharged into fractionator 24 by way of line 22 containing control valve 23.

Depending upon the amount of dissolved gases and high vapour pressure material present, the pressure in the stabilising tower may be varied from approximately 125 to 175 pounds per square inch and the temperature at the vapour inlet  
85 from 125 to 200°F. It is current practice to maintain a temperature of approximately 125°F. at the top of the stabilising tower by recirculation of overhead condensate and a temperature of 350°F. at  
90 the bottom of the tower by means of some type of reboiler such as a closed coil through which hot residuum from the cracking step is passed. The vapours from the fractionator comprising principally  
95 methane, ethane, propane and butanes and corresponding unsaturates pass through line 25 containing control valve 26 and a definite proportion of the hydrocarbons are liquefied during passage  
100 through condenser 27 which may be operated if desired, at sub-atmospheric temperatures to insure the collection of more distillate. Liquids and gases flow from the condenser through line 28 containing  
105 control valve 29 to receiver 30 having fixed gas release line 31 containing control valve 32 and a liquid draw line 33 containing control valve 34 through which the low boiling liquids produced at this point  
110 may be withdrawn and stored either for blending or ultimate disposal as domestic fuel. To control the composition of the effluent vapours from the stabiliser a portion of the condensed liquid is returned  
115 to the top of the stabilising tower by way of line 35, control valve 36, recirculating pump 37, line 38 and control valve 39.

The stabilised naphtha is now subjected in liquid phase to treatment with fullers  
125 earth, clay or other suitable adsorptive catalysts. The temperatures employed in the clay treating step may range from approximately 300—450°F., and if added heat is necessary to obtain the proper  
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treating temperature, it may conveniently be obtained through indirect heat exchange with the bottoms from either the primary or secondary cracking plant fractionators, for example, the secondary tower shown at 3 in the drawing. Thus, in the present hook-up bottoms are taken by a pump 92 through liquid drawoff line 90 containing control valve 91 and discharged by way of line 93 containing control valve 94 through a heat exchanger 45<sup>1</sup> which may be of any suitable type, the drawing showing the fractionator bottoms flowing through an interior closed coil. The stabilised distillate is withdrawn from tower 24 through a line 40 containing control valve 41 and picked up by a pump 42 which discharges through line 43 containing control valve 44 to the heat exchanger 45<sup>1</sup>. The heated distillate then leaves the heat exchanger by way of line 45 containing control valves 46 and 47 to undergo clay treatment. The pressure at this point necessary to insure substantial liquid phase conditions in the treating step following will depend upon the vapour pressure of the distillate, and may be considerable, sometimes as high as 300 to 400 pounds per square inch, when using the higher range of temperatures.

The clay treaters are preferably arranged so that they may be employed in series or parallel and so that either up or down flows may be employed. In the drawing any number of interconnected treating towers are represented by towers 64 and 68 which contain stationary bodies of adsorptive earth or the like solid active adsorbent 65 and 69 respectively. These stationary solid active adsorptive masses are supported upon perforated screens and upper screens are also provided to prevent the floating away of the particles if up-flows are used. In treater 64, 67 represents a supporting screen and 66 an upper retaining screen while in treater 68, 71 represents the lower screen and 70 to the upper.

The fineness of the clay particles employed in the treaters is usually included between 10 and 60 mesh though the size may be varied to effect a practical balance between the treating effect and the resistance to flow.

To effect a down-flow series treatment the distillate in line 45 is passed through the clay bed in treater 64 from line 48 with valves 49 and 50 open, while valve 52 in line 51 and valves 47 and 58 in line 45 are closed. The effluent from the tower passes through line 55 containing control valve 56, valve 57 in line 45 and follows line 60 through valve 61 to line 51 in which valve 53 is open and valve 54 is closed. The liquid thus follows line 62 con-

taining control valve 63, passes through the clay bed in treater 68 and then through line 72 containing control valve 73, valve 59 in line 45 and valve 74 in line 51.

For parallel or split-down-flows valves 50, 63, 56, 57, 58, 59 and 73 are opened while valves 47, 61 and 54 are closed. The amount of liquid passing through the different towers may be controlled by the manipulation of these valves.

For a series up-flow treatment the following valves will be opened: 47, 56, 50, 52, 61, 58, 73, 63 and 54, while the following valves will be closed: 49, 57, 53 and 59.

For parallel or split feed up-flow treatment the following valves will be open: 47, 56, 57, 58, 73, 50, 52, 53, 63 and 54, while the following valves are closed: 49, 61 and 59.

The clay treated material is now finally fractionated to produce treated and stabilised gasoline and in case more heat is necessary for the final fractionation it may be conveniently obtained by further heat exchange from cracking plant tower bottoms, the drawing showing the utilisation of the partially cooled bottoms from the closed coil in heat exchanger 45<sup>1</sup>, which pass through line 95 containing control valve 96 to heat exchanger 97 and leave through line 98 containing control valve 99. The distillate from the clay treaters leaves the heat exchanger 97 by way of line 75 containing control and pressure reducing valve 76 and enters a final fractionator 77 which may conveniently be operated within about the same pressure range as that used in fractionator 3. The bottoms from this fractionator are withdrawn through line 88 containing control valve 89 and used as a portion of the combined feed to the cracking plant. The vapours of the desired gasoline product leave through line 78 containing control valve 79 and are condensed during passage through condenser 80, flowing therefrom through line 81 containing control valve 82 to receiver 83 which is provided with a conventional gas release line 84 containing control valve 85 and a liquid draw line 86 containing control valve 87 through which the gasoline may be passed to storage. The final product may then be sweetened by the conventional caustic or plumbite treatment or in any desired manner.

The following example of results obtainable by the use of the present process will serve to indicate its commercial value although the scope of the invention is not to be limited thereto.

To produce a distillate for treating by the present process a gas oil distillate was

cracked at a temperature of approximately 950°F., and a pressure of about 500 pounds per square inch. The properties of the distillate are given in the following

5 table:

PROPERTIES OF CHARGING STOCK.				
10	Gravity, °A.P.I.	-	-	36.9
	Sulphur, %	-	-	0.25
	100 cc. A.S.T.M. Distillation			
	I.B.P. °F.	-	-	250
	5%	-	-	304
	10	-	-	319
	20	-	-	343
	30	-	-	359
	40	-	-	375
	50	-	-	392
15	60	-	-	410
	70	-	-	429
	80	-	-	454
	90	-	-	492
20	E.P. °F.	-	-	563
	% Over	-	-	99.0
	% Bottoms	-	-	1.0
	% Loss	-	-	0.0

The cracking yields, expressed in volume % of the charging stock were as follows:

25	Gasoline	-	-	61.1%
	Residuum	-	-	15.2%
	Gas and loss (by difference)	-	-	23.7%

The gasoline was stabilised to ten pounds vapour pressure and then passed through 60 to 90 mesh fullers earth at a temperature of approximately 362°F., and a pressure of about 250 pounds per square inch. The following table shows the properties of the untreated gasoline in column 1 and the product after stabilisation and hot clay treatment in column 2. There was a loss of 1.7% in the stabilisation step and a loss of 1% in the hot filtering step due to polymerisation.

PROPERTIES OF RAW AND TREATED GASOLINE.				
45		1	2	
	Gravity °A.P.I.	53.7	50.8	
	Colour, Saybolt	-3	+30	
	Colour stability	-	25	
	Doctor test	pos.	pos.	
	Mg. of gum/100 cc.			
	by copper dish	8	1	
	Sulphur %	0.12	0.10	
	Induction period in oxygen bomb, Min.	75	45	
	Induction period in oxygen bomb, Min. with inhibitor*	220	505	
50	Octane number (motor method)	77	77	
	Initial boiling point, °F.	96	132	
	5% over at °F.	131	156	
	10% over at	154	174	

20% over at	-	-	190	202	65
50% over at	-	-	258	256	
90% over at	-	-	318	309	
End point, °F.	-	-	346	335	

\*The untreated sample received 0.075% and the treated sample 0.025% of wood tar inhibitor.

The effects of the treatment are evident from a consideration of the above data. By the combined steps of stabilisation and hot clay filtering the colour is raised, and the gum and sulphur content is lowered. Although the induction period after treatment was slightly lower, there was evidently a greater inhibitor susceptibility since a smaller amount of inhibitor produced a much greater increase in the induction period. The anti-knock value was unaffected. The sweetening of the treated gasoline was effected by a light treatment with sodium plumbite.

The nature of the present invention and its value in practice will be readily seen from the preceding specification and the numerical data, neither of which, however, are to be considered as imposing exactly corresponding limitations upon the scope of the invention.

Having now particularly described and ascertained the nature of my said invention and in what manner the same is to be performed, I declare that what I claim is:—

1). A process for refining cracked hydrocarbons of substantially gasoline boiling range by the treatment with a solid active adsorbent such as fullers earth under conditions of elevated temperature and superatmospheric pressure adequate to maintain said hydrocarbons in substantially liquid phase, which comprises first removing from said hydrocarbons relatively unstable low boiling constituents, namely dissolved gases, propane, part or all of the butanes and their corresponding unsaturates, and reducing the vapour pressure of said hydrocarbons by submitting them to a stabilising fractionation and thereupon subjecting the stabilised hydrocarbons, whilst still hot, to said refining treatment.

2). Process as set forth in claim 1, in which the stabilising fractionation is combined with a fractionation for producing the hydrocarbons of substantially gasoline boiling range from vapours from a cracking operation and in which the stabilised hydrocarbons are removed as hot condensate from an intermediate point of the combined fractionation.

3). Process as set forth in claim 1, in which the stabilising fractionation is effected separately from the fractionation for producing the hydrocarbons of substantially gasoline boiling range from vapours

of a cracking operation.

4). Process as set forth in claim 3, in which heavier reflux fractions obtained in the fractionation for producing the hydrocarbons of substantially gasoline boiling range are returned to further conversion, whilst said hydrocarbons are condensed, uncondensed gases are separated and the condensate is thereupon subjected to re-vaporisation and stabilising fractionation under pressure.

5). Process as set forth in any of the preceding claims, in which the action of the solid active adsorbent on the stabilised hydrocarbons is effected at a temperature of from 300 to 450°F., and under a super-atmospheric pressure of about 250 pounds or more, per square inch.

6). Process as set forth in any of the preceding claims, in which the stabilised hydrocarbons, after having been subjected to the action of the solid active adsorbent, are revaporised by reduction of pressure and additional heating and are fractionated to separate polymers therefrom and to produce an overhead refined product of substantially gasoline boiling range, which is cooled, condensed and collected.

7). Process as set forth in any of the preceding claims, in which an overhead product obtained by the reduction of pressure and revaporisation of the stabilised hydrocarbons is subjected to the action of a sweetening agent, preferably comprising sodium plumbite.

8). Process as set forth in any of claims 4 to 7 in which the stabilised hydrocarbons before being subjected to the action of the solid active adsorbent, are heated to the desired temperature by indirect heat exchange with a heating fluid, preferably with reflux condensate obtained during the fractional separation of the cracked hydrocarbons prior to stabilisation.

9). Process as set forth in any of claims 4 to 8, in which the stabilised hydrocarbons, after having been subjected to the action of the solid active adsorbent, are heated by indirect heat exchange with a heating fluid, preferably with reflux condensate obtained during the fractional separation of the cracked hydrocarbon prior to stabilisation, to a temperature sufficient to effect their revaporisation and final fractionation.

10). Apparatus when used for carrying out the process of claims 1—9, which comprises a stabiliser-fractionator for separating relatively low boiling cracked hydrocarbons into an intermediate stabilised fraction of substantially gasoline boiling range and into relatively unstable low boiling constituents, one or more treating chambers containing a solid active adsorbent, and adapted to with-

stand a superatmospheric pressure sufficient for maintaining the stabilised intermediate fraction in substantially liquid phase during its treatment with said active adsorbent, a conduit for supplying the intermediate stabilised fraction from said stabiliser fractionator to said treating chamber or chambers and containing a pump and a heat exchanger, if desired, a final fractionator for the separation of polymers and final fractionation of the refined stabilised intermediate fraction, a conduit provided with a pressure reducing valve making communication between said treating chamber or chambers and said final fractionator, and means for condensing and collecting the refined stabilised overhead product of said final fractionator.

11). Apparatus when used for carrying out the process of claims 1—9, which comprises a fractionator for separating from cracked hydrocarbons an overhead product, consisting largely of constituents of gasoline boiling range, and a heavier reflux fraction, means in communication with said fractionator for condensing and collecting said overhead product, with or without means for removing fixed gas from said collecting means, a heating device for revaporising said condensed overhead product, a stabiliser fractionator in communication with said heating device for removing gases and relatively unstable low boiling components from said overhead product and for reducing the vapour pressure thereof, one or more treating chambers, containing a solid active adsorbent in communication with said stabiliser-fractionator by means of a conduit containing a pump and a heat exchanger, if desired, said treating chamber being adapted to withstand the super-atmospheric pressure required for maintaining the stabilised product in substantially liquid phase during its treatment with said solid active adsorbent, a final fractionator, a conduit provided with a pressure reducing valve making communication between said treating chamber or chambers and said final fractionator, and means for condensing and collecting the refined stabilised overhead product of said final fractionator.

12). Apparatus as set forth in claim 10 or 11, in which a heat exchanger is provided in the conduit leading from the treating chamber or chambers to the final fractionator.

13). A process of refining low boiling cracked hydrocarbons substantially as described, and for the purpose set forth.

14). An apparatus for refining low boiling cracked hydrocarbons, substantially as described and illustrated with re-

ference to the accompanying drawings.

15). Stabilised refined hydrocarbons  
for use as/or in gasoline whenever pro-  
duced by the process set forth in the  
5 claims 1—9.

Dated this 18th day of April, 1934.

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[This Drawing is a reproduction of the Original on a reduced scale.]

